ACTIVITY REPORT

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Natural Gas & Oil Technology Partnership

bringing department of energy national laboratories capabilities to the petroleum industry

Los Alamos
Los Alamos, NM 87545
(505) 667-3595

Sandia
Albuquerque, NM 87185
(505) 844-7333

Lawrence Livermore
Livermore, CA 94551
(925) 422-5196

Lawrence Berkeley
Berkeley, CA 94720
(510) 486-5961

Argonne
Argonne, IL 60439
(202) 488-2415

Brookhaven
Upton, NY 11973
(631) 344-3819

Idaho
Idaho Falls, ID 83415
(208) 526-7004

Oak Ridge
Oak Ridge, TN 37831
(865) 574-4977

Pacific Northwest
Richland, WA 99352
(509) 376-2342

To: William F. Lawson, Director
National Petroleum Technology Office
U.S. Department of Energy
P.O. Box 3628
Tulsa, OK 74101

From: E.M. Whitney, Los Alamos
D.J. Borns, Sandia
F. Followill, Lawrence Livermore
N. Goldstein, Lawrence Berkeley
D. Schmalzer, Argonne
A. Goland, Brookhaven
C. Thomas, Idaho
T. Schmidt, Oak Ridge
B. Saffell, Pacific Northwest

cy: G. Dehoratiis, DOE Fossil Energy
E. Allison, DOE Fossil Energy
A. Hartstein, DOE Fossil Energy
B. Hochheiser, DOE Fossil Energy
G. Stosur, DOE Fossil Energy
E. Subia-Melchert, DOE Fossil Energy
S.L. Waisley, DOE Fossil Energy
W. Polansky, DOE Office of Science
N.B. Woodward, DOE Office of Science
D. Alleman, DOE-NPTO-Tulsa
J. Casteel, DOE-NPTO-Tulsa
N. Comstock, DOE-NPTO-Tulsa
B. Lemmon, DOE-NPTO-Tulsa
R. Lindsey, DOE-NPTO-Tulsa
D. Sutterfield, DOE-NPTO-Tulsa
J. Ammer, NETL
F. Brown, NETL
H. Guthrie, NETL
B. Gwilliam, NETL
R. Long, NETL
B. Tomer, NETL
A. Yost, NETL

Note: Natural Gas and Oil Technology Partnership projects are reported according to the following schedule:

January, March, May, July, September, November	**February, April, June, August, October, December**
Oil and Gas Recovery Technology Drilling, Completion, and Stimulation Technology Diagnostic and Imaging Technology	Upstream Environmental Technology Downstream Environmental Technology

Natural Gas and Oil Technology Partnership on the World Wide Web: http://www.sandia.gov/ngotp/

Upstream Environmental Technology

Continuous Monitoring of Particulate Matter and Particulate Matter Precursor Emissions from Stationary Sources (Chevron and SNL)

Project is in close-out phase.

Development of an In-Well Oil/Water Separator for *In Situ* Recycling of Produced Water (Baker Hughes, Chevron, CINC, Oak Ridge Tool & Engineering, Phillips, REDA Pump, Texaco, Unocal, and ORNL)

Highlight:

- New housing for centrifugal separator constructed.

Bench-scale testing has been halted until the modified equipment has been manufactured.

Last year, solids, water, and oil were separated using a hydrocyclone in combination with the centrifugal separator. The system worked very well when the solids had been removed in the hydrocyclone, producing a clean split of oil and water in the separator. The system was operated for a short time (approximately 1 hour). Adjustments were made to the hydrocyclone/separator system so that long-term (6–8 hours) operation is possible.

The housing for the separator was redesigned and will be machined in Plexiglass. The new housing will accept a longer rotor, which will allow for increased throughput capacity. The portion of the rotor housing that controls the flow of the separated streams was also redesigned not to protrude from the sides but to run down the side. Exchangeable parts of the housing were designed to allow for adjustment of the collection well volumes.

Stationary Source Emission Control Using Plasma-Assisted Catalysis (Cummins Engine, Edison Chouest Offshore, and LLNL)

Project is in close-out phase.

Reducing Chemical Use and Toxicity in Produced-Water Systems (BP Amoco, Rhorback Casasco Systems, and ANL)

Highlight:

- New software package for automatic on-line ECN monitoring tested.

The new user-friendly software package for automatic electrochemical noise measurement and data interpretation was used to detect pitting corrosion in experiments using ANL's laboratory flow loop system. The electrochemical noise (ECN) measurement experiments included the evaluation of optimal electrode design in both a microbially influenced corrosion (MIC) and chemical corrosion (CC) environment. The later experiment was designed to determine whether any distinguishable difference could be seen between the MIC and CC ECN signal patterns. The flow loop used to evaluate the optimal electrode design for the MIC was filled with simulated produced water. Three ECN probes with electrodes of different degrees of surface roughness were inserted in the loop. Four metal coupons were also put into the loop to measure bacterial colonization by physical examination of the metal surface under an optical microscope. The CC flow loop was filled with 1 percent sodium chloride solution. Two ECN probes with the modified electrodes were placed in the loop. Four coupons were also inserted in the CC loop to validate the general corrosion rate under CC attack. The ECN measurement experiments in both flow loops are still in progress.

The new software package has been operated continuously for more than 400 hours without any corruption of the ECN signal. Preliminary results

indicate that high-order statistical analysis of the ECN signal may possibly be used to differentiate MIC from CC attack. Specifically, the Kurtosis indices of the average potential of the ECN probes in the MIC environment have much higher values than the ECN probes in the CC environment. This may occur because the Kurtosis analysis is used to characterize the relative peaks or flatness of a distribution, as compared to normal distribution of the signal. The colonization of bacteria on the metal surface during the MIC attack may create much more volatile potential signals compared to the relatively smooth surface coverage of corrosion products on the metal surface in the CC environment. Validation of this basic finding is being accomplished by reanalyzing the large number of ECN signal records that were created in our previous experiments. Modification of the software package to incorporate the *in situ* Kurtosis analysis is planned.

Sulfide Removal in Produced Brines by Microbial Oxidation

(Phillips, U of Tulsa, and INEEL)

Highlights:

- Results favorable from water chemistry and biological analyses.
- Completed bioreactor design for field-specific implementation.
- Determined impact of site-specific conditions on selected microbial cultures.

Comparative experiments between *Thiobacillus denitrificans* and CVO (Coleville organism) are nearing completion. Current results were announced at the Partnership meeting held in Tulsa, OK, held January 17. Briefly highlighted were similarities and differences between CVO and *T. denitrificans* (operating in bioreactors). Given the current results and known information from the selected field-application site, *T. denitrificans* is the logical choice as a biocatalyst. Both systems exhibited significant free cell populations necessary for complete hydrogen sulfide (H_2S) removal (only the outermost region of Bio-Sep beads occupied by organisms). In summary, conclusions for conditions tested were that *T. denitrificans* exhibited greater H_2S removal efficiency, greater biomass yield on H_2S, better restart characteristics, and slightly better tolerance of accumulating sulfate. In both systems, H_2S was oxidized completely to sulfate, and 1.6 moles nitrate were required per mole of H_2S.

Preparation for field demonstration continues. The University of Tulsa is beginning to iterate design criteria with a fabricator in Tulsa for final cost estimation of equipment for deployment.

Characterization of Soluble Organics in Petroleum Waste Water

(Chevron, Marathon, Phillips, Shell, Statoil, and ORNL)

ORNL is identifying water soluble organics (WSO) in produced water derived from Gulf of Mexico (GOM) crude oil/brine contacts. A number of contact experiments were performed to determine the influence of the percent water/oil cut, pH, salinity, temperature, and pressure on the quantity of extractable organics found in GOM brine.

Polar organic compounds comprise the majority of WSO found in treated brine. Efforts are being directed toward determining the mass of WSO derived from small organic acids (C_1–C_6) as opposed to polar petroleum hydrocarbons. Concentrations of organic acids are being determined by injecting treated brines into an ion chromatograph fitted with an IonPac ICE-AS6 (Dionex Corp.) separation column. The acids are separated from the high-chloride sample matrix using a 0.4 µm heptafluorobutyric acid eluent; a 1 ppm detection limit is typical. Organic acids identified thus far include formic, acetic, and proprionic, present at levels of less than 20 ppm. This result compares to total petroleum hydrocarbon concentrations of 20–30 ppm. When all samples have been analyzed, ion chromatographic results will be correlated with experimental conditions to determine the primary mechanism controlling WSOs derived from organic acids.

Ecological Framework to Evaluate the Effect of Size and Distribution of Releases at Upstream Petroleum Sites

(American Petroleum Institute, BP Amoco, Chevron, Exxon, Gas Technology Institute, Texaco, Unocal, LBNL, ORNL, and LLNL)

Highlights:

- Presentation made at the Upstream Environmental Technology review meeting.
- Paper presented at SPE meeting.
- Presentation made at the PERF 99-13 kickoff meeting.

LLNL and ORNL presented project progress to date at the annual Upstream Environmental Technology review, held January 17, at the NPTO offices in Tulsa, OK. All major milestones for the project are expected to be met for the FY00 funding, and milestones for FY01 funds have been prepared. Tina Carlsen, of LLNL, presented an invited symposium paper at the Society of Petroleum Engineers Upstream Environmental meeting on February 26 in San Antonio, TX. The paper, co-authored by ORNL and entitled "Current directions in screening-level ecological risk assessments," was described in the December 2000 *Activity Report.* The presentation was well received, and there were numerous requests for copies. Tina Carlsen and Rebecca Efroymson, of ORNL, also attended the PERF 99-01 (Petroleum Environmental Research Forum) kickoff meeting, "Expanding the Science Basis for Risk," in February. Rebecca agreed to lead the ecological work group for this new PERF initiative.

LLNL completed a draft review of models potentially relevant to animals in patchy, terrestrial landscapes. Models described include (1) those used to model changes in the physical landscape, (2) population models using probabilistic state variables (random sample hypothesis, metapopulation and probability distribution models), (3) models with aggregated state variables (source-sink, constant density, evolutionarily stable strategy, game theory, resource depletion, and population dynamic models), and (4) models with individuals as state variables. This review, along with that prepared by ORNL on population viability analysis, will be used in developing a project modeling plan.

LLNL also completed a draft review of field and experimental data on critical patch size for actual species. The review is a series of tables describing critical patch-size and home-range data. LLNL also finalized the Tall Grass Prairie trophic model. The trophic model and the critical patch-size data will be used to assist selection of end-point species to be modeled.

The national laboratories continue to identify and collect map layers for the geographic information system that will support the modeling effort at Oklahoma's Tall Grass Prairie Preserve. The first version of the Geographic Information Systems (GIS) data collection protocol authored by LLNL is being finalized. LLNL completed a mock up of the GIS WEb site, which is currently undergoing review and release. ORNL completed a normalized difference vegetation index (NDVI) time series of maps for the Tall Grass Prairie Preserve. These maps, based on remotely sensed imagery, are indicators of the biomass of vegetation at the site. ORNL visited the U.S. Department of Agriculture's Jornada Agricultural Experimental Station, where in June 2000, a road grader drove over a diesel pipeline, releasing about 75,000 gallons over about 5 acres. ORNL is exploring the use of this data-rich site.

Estimation and Reduction of Air Quality Modeling Uncertainties

(Envair, EPRI, and LBNL)

Highlight:

- Initial version of uncertainty framework constructed.

LBNL researchers made considerable progress on a paper describing an early application of exercising the framework. The application is associated with evaluating the accuracy of an important model improvement concerned with the framework's photochemistry.

Nancy Brown, the project's principal investigator, presented a project review to DOE and industry representatives at the NPTO office in January.

Remote Sensing for Environmental Baselining and Monitoring

(Chevron, UC-Davis, and ORNL)

Highlight:

- Field site visited.

A field-site visit was made to the Jornada Experimental Range near Las Cruces, NM. The site has been operated by the U.S. Department of Agriculture, Agricultural Research Service, since 1915.

In June 2000, a road grader penetrated an oil pipeline. The ruptured pipeline sprayed an estimated 75,000 gallons of diesel oil into an experimental area. The spray covered about 5 acres; the spill covered about 2 acres. The spill caused extensive damage to area flora, consisting of 50–60-year-old creosote bushes (*Larrea tridentata*) in the upper canopy and Bush muhly (*Muhlenbergia porteri*) in the lower canopy. The impacted shrubs are white and withered, and the grasses are yellowish golden in color.

In September 2000, NASA collected remote hyperspectral data by flying the AVRIS (Airborne Visible Infrared Imaging Spectrometer), (224-band) sensor over Jornada. NASA will re-fly the area in May. ORNL has ordered a 512-band field spectroradiometer from Analytical Spectral Devices and plans to collect field hyperspectral data at Jornada this spring.

Downstream Environmental Technology

Bioprocessing of High-Sulfur Crudes via Application of Critical Fluid Biocatalysts

(Texaco, UOP, and INEEL)

Highlights:

- Enzymatic reactions conducted as base comparisons.
- Control experiment conducted.

Work exploring biocatalysis in organized media—including reverse micelles, microemulsions, and emulsions—began in January.

Initial work explored the bioxidation of dibenzothiophene (DBT) in AOT reverse micelles. The reaction was carried out at 40°C and 2,100 psi for two hours in supercritical ethane using 1-octanol as a co-surfactant and Cytochrome c (Cyt c) as the biocatalyst. A clear phase was visually observed after pressurizing with ethane, before protein addition, suggesting that reverse micelles were formed. However, at the end of the reaction some white solid was observed on the window, suggesting that either some AOT or some protein precipitated during the reaction. The reverse micelle reaction resulted in no conversion to product.

It was determined that the AOT co-surfactant 1-octanol is an inhibitor for the Cyt c biocatalyst. Additional liquid phase tests determined that ethanol and 1-butanol did not inhibit the biocatalyst and potentially could be used as a co-surfactant; however, 1-hexanol did inhibit the biocatalyst. Without the co-surfactant, only small amounts of water can be used with supercritical ethane.

Work is focusing on a new perfluoropolyether (PFPE) surfactant. The PFPE surfactant does not require a co-surfactant when used in supercritical carbon dioxide. The surfactant was synthesized and tested under both liquid phase and supercritical conditions. The hemoglobin catalyzed oxidation of DBT in liquid ethanol was found to proceed, but the yield was lower in the presence of the PFPE surfactant. Control experiments using supercritical carbon dioxide, surfactant, water, buffer, and hydrogen peroxide demonstrated that at 40°C and 3,300 psi, a single fluid phase is generated. Initial oxidation experiments using hemoglobin in supercritical carbon dioxide microemulsions have been performed; however, the results are still inconclusive.

A cooperative research and development agreement with Texaco is being finalized.

Biological Upgrading of Heavy Oils for Viscosity Reduction

(BP Amoco, Chevron, EPRI Chemicals, Natural Gas Center, Texaco, and LBNL)

The objective of this study is to develop novel biocatalytic agents for viscosity reduction of heavy oils. High-viscosity crude oils are much more expensive to produce, transport, and process than less viscous oils. Alkane oxidases are known to catalyze alkanes, which constitute a major portion of heavy oils, and to produce corresponding alcohols that reduce the viscosity of these oils. Bacterial cultures will be isolated and examined for their ability to convert higher alkanes to alcohols.

Researchers at LBNL isolated 42 pure bacterial strains from an octane-degrading mixed culture and dozens of isolates from cultures grown on both lower and higher alkanes such as isopentane, decane, dodecane, hexadecane, and tetradecane. Colony morphology indicates that there are at least ten different types of organisms. These organisms are being tested for their ability to oxidize diverse alkanes and their degradation kinetics, and will be identified through 16s RNA analysis to achieve higher degree of accuracy on their phylogenic uniqueness. Among these organisms, nine strains were examined to determine the presence of the alkane hydroxylase (AlkB) in their genes through polymerase chain reaction amplification using degenerative primer, TS2S and deg1RE. Two organisms did not show any correspondence with the AlkB gene, indicating these two strains might have a unique alkane degradation pathway compared to previously known alkane degradation mechanisms. Further study will confirm metabolic diversity of isolated organisms and select organisms showing the best biocatalytic traits. The project is on schedule.

Kinetics of Biochemical Upgrading of Petroleum

(Biocat, Chevron, Shell, and BNL)

No report received.

Enzymatic Upgrading of Heavy Crudes via Partial Oxidation or Conversion of PAHs

(Chevron, Phillips, Texaco, ORNL, and INEEL)

The first experiment to produce a population of mutated lignin peroxidase gene (lip), using error-prone polymerase chain reaction (PCR) and primers containing two restriction sites, *SfiI* and *XhoI*, was completed. Upon transferring the mutated genes into a DH5a strain, it was found that either the gene could not be inserted in the correct orientation, or the plasmid could not be maintained stably. This failure may have been because of the relatively large size of the *SfiI* restriction site or from unknown effects caused by the mutations in the gene. Therefore, an alternate restriction site—*EcoRI*, which is only six bases long—was chosen for further mutations. Using primers inclusive of this site, ORNL has gone through the complete cycle from creation of mutations in the gene via error-prone PCR to transformation of the mutant genes, first into *E. coli* and then into *Pichia pastoris*. The first attempt has produced about 20 clones each, in two different strains. Researchers are assessing these clones for LiP activity.

Improvements in enzymatic activity via chemical modification of the enzymes were reported previously. To assess the extent and location of chemical modification, researchers are analyzing modified enzymes via polyacrylamide gel electrophoresis and thin-layer chromatography. The additional information obtained will provide fundamental insight into enzyme-substrate binding and may assist in proving the hypothesis explaining low activity in solvents because of thermodynamic limitations.

Due to a reduction in the funding level for FY01 on this project, some of the tasks for this year will have to be postponed until next year. An updated milestone schedule will be prepared for discussion with the industry participants and DOE in the next review meeting.

A Predictive Model of Indoor Concentrations of Outdoor $PM_{2.5}$ in Homes

(Aerosol Dynamics, Envair, Western States Petroleum Association, and LBNL)

Highlight:

- Completed winter intensive-measurements suite at Fresno Field Site.

Participants completed the winter season measurements program. LBNL is preparing three scientific papers for publication. Topics are the ammonia measurement system, the deposition and penetration processes, and the differences between indoor and outdoor NH_4NO_3 particle concentrations.

Real-Time Characterization of Metals in Gas and Aerosol Phases

(BP Amoco, Equilon, Marathon, Phillips, Shell, Eastman Chemicals, and ORNL)

Highlights:

- Entered final phase of field testing.
- Conference paper accepted.

The project has entered its final phase of field testing of the prototype instrument for low-level emissions of metals. The instrument combines aerosol focusing technology with laser-induced plasma spectrometry in a field-portable package. Tests are ongoing at the diesel engine research facility at ORNL using high- and low-sulfur fuels as well as different engine operating conditions. Preliminary data indicate that the background gases (e.g., those resulting from different fuels burned) interfere little with detection. Detailed data analysis will be performed after the test is completed in a few weeks. Another field test is planned for spring. This test was suspended because the Eastman contact left the project.

A conference paper has been accepted and will be presented at the annual meeting of the Air and Waste Management Association in June.

Partnership Office

Partnership funding recommendations for the FY01 Upstream Environmental Technology area were developed based on the results of the Industry Review Panel meeting held January 17 in Tulsa, OK. The NPTO accepted the recommendations and has requested that the labs submit appropriate Field Work Proposals by March 12 for DOE funding actions.